Supplementary Information:

Site-Selective Localization of Analytes on Gold Nanorod Surface for Investigating Field Enhancement Distribution in Surface-Enhanced Raman Scattering

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1. Synthesis of Au nanorods

Au nanorods (AuNRs) with aspect ratio of about 2.5 were synthesized by using the reported method.[1] For the following calculations, AuNRs were considered as a cylinder (diameter and length of 22.3 ± 3.4 and 40.9 ± 2.6 nm) with two spherical crown (height and diameter are 7.3±1.6 and 22.3±3.4 nm), Figure 1d.

2. Synthesis of 36 nm gold nanospheres by using seed-mediated growth method

Seed solution (17 nm gold nanospheres, AuNSs) was prepared using the reported method.[2] Briefly, 10 mg of $HAuCl_4 \cdot H_2O$ was firstly dissolved in 100 mL H_2O and was heated at 110 ^oC for 15 min. After that, 3 mL sodium citrate (1%, w/w) was added to the solution, followed by heating to another 30 min, then cooling down to room temperature. For preparing 36 nm AuNSs, 10 mg of $HAuCl_4 \cdot H_2O$ was firstly dissolved in 100 mL H_2O and was heated at 110 ^oC for 15 min, then adding 10 mL seed and 400 μL sodium citrate solution (1 %, w/w in water) simultaneously, heating at 110 ^oC for another 30 min and then cooling down to room temperature.

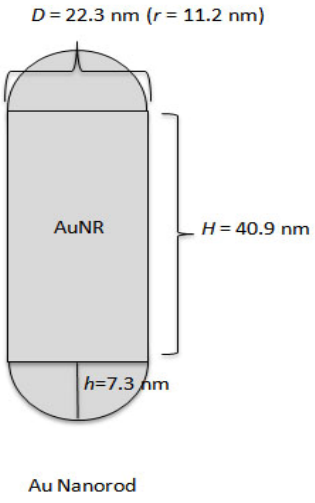
3. A typical procedure of enhancement factor calculation

h = 7.3 nm, r = 11.2 nm, H = 40.9 nm,

Molecular weight of $HAuCl_4 \cdot H_2O$ is 339.79+18 =357.79 g/mol

Percentage of Au: 196.97/357.79=0.5505.

The volume of one gold nanorod:



Au Nanorod

$$V_{cap} = \pi h(3r^2 + h^2)/6$$
$$= 3.14 \times 7.3 \times (3 \times 11.2^2 + 7.3^2)/6$$
$$= 1.641 \times 10^3 nm^3$$
$$V_{cylinder} = \pi r^2 h = 3.14 \times 11.2^2 \times 40.9 = 1.611 \times 10^4 nm^3$$
$$V_{NR} = 2V_{cap} + V_{cylinder} = 1.939 \times 10^4 nm^3$$

Weight of the Au in the growth solution:

$$W_{Au} = 5 \times 10^{-5} mol \times (339.79 + 18) \times 0.5505 = 9.848 \times 10^{-3} g$$

$$V_{solution} = 100.675 ml$$

Weight of one AuNR:

$$V_{NR} = 1.939 \times 10^4 nm^3$$
$$Density = 19.32 g.cm^{-3} = 19.32 \times 10^{-21} g.nm^{-3}$$
$$W_{NR} = 1.939 \times 10^4 \times 19.32 \times 10^{-21} = 3.746 \times 10^{-16} g$$

100.675 mL solution contains AuNR:

$$N_{NR} = \frac{9.848 \times 10^{-3}}{3.746 \times 10^{-16}} = 2.630 \times 10^{13}$$

1 mL solution contains AuNR:

$$N_{1mL} = 2.612 \times 10^{11}$$

Concentration of as-synthesized AuNRs:

$$C_{AuNRs} = \frac{2.612 \times 10^{11}}{6.02 \times 10^{23}} \times 10^3 = 4.339 \times 10^{-10} M = 0.4339 nM$$

Concentration of SERS experiment:

$$C_{SERS} = 0.238 nM$$

$$(\frac{0.4339 nM \times 1.5 mL}{1 mL} \times \frac{2}{5} / 1.1 mL = 0.237 nM)$$

Surface areas of AuNRs:

$$S_{cap} = 2\pi Rh = 2\pi \frac{h^2 + r^2}{2h} \times h = \pi(h^2 + r^2)$$
$$= 3.14 \times (7.3^2 + 11.2^2) = 561.2nm^2$$
$$2S_{cap} = 1122.4nm^2$$

$$S_{cylinder} = 2\pi rh$$
$$= 2 \times 3.14 \times 11.2 \times 40.9 = 2876.7nm^2$$

Total surface area of one AuNR:

$$S_{NR} = 3.999 \times 10^3 nm^2$$

Enhancement Factors (Abased on the data showing in Figure 1 in the main text):

Since the shape of the same Raman peaks remain nearly the same in the characterizations, we compared the peak heights in the data analysis.

$$EF = \frac{I_{SERS}}{I_{Bulk}} \times \frac{N_{Bulk}}{N_{SERS}} = \frac{I_{SERS}}{I_{Bulk}} \times \frac{C_{Bulk} V_{Bulk} N_A}{C_{SERS} V_{SERS} N_A} = \frac{I_{SERS}}{I_{Bulk}} \times \frac{C_{Bulk}}{C_{SERS}}$$

*SERS analyte-**3** (4-MBA):*

$$EF_{3(all)} = \frac{669 - 291}{256 - 208} \times \frac{0.01}{0.237 \times \frac{3.999 \times 10^3}{0.20} \times 10^{-9}} = 1.66 \times 10^4$$

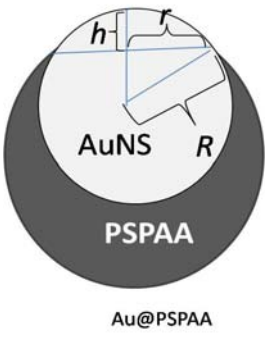
$$EF_{3(end)} = \frac{525 - 246}{256 - 208} \times \frac{0.01}{0.237 \times \frac{1122.4}{0.2} \times 10^{-9}} = 4.37 \times 10^4$$

Gold Nanospheres, *R* = 36.0 nm

Growth solution: 89 mL water and $HAuCl_4 \cdot H_2O$ (1 mL, 10 mg/mL in H_2O)

Seed: 10 mL of 17 nm AuNSs

Total Au precursor: 11 mg; total volume of AuNPs solution: 100mL



Au@PSPAA

$$V_{AuNS} = \frac{4}{3}\pi r^3 = \frac{4}{3} \times 3.14 \times 18^3 = 2.44 \times 10^4 nm^3$$
$$S_{AuNS} = 4 \times 3.14 \times 18^2 = 4.07 \times 10^4 nm^2$$

Weight of one AuNS:

$$W_{AuNS} = 2.44 \times 10^4 \times 19.32 \times 10^{-21} = 4.71 \times 10^{-16} g$$

Number of AuNSs in 100 mL solution:

$$N_{100mL} = \frac{W_{Au}}{W_{AuNS}} = \frac{11\times10^{-3}\times0.5505}{4.07\times10^{-16}} = 1.49\times10^{13}$$

The number of AuNSs in 1 mL solution:

$$N_{1mL} = \frac{1.49\times10^{13}}{100} = 1.49\times10^{11}$$

Concentration of AuNSs:

$$C = \frac{1.49\times10^{11}}{6.02\times10^{23}}\times10^{3} = 2.48\times10^{-10}M = 0.248nM$$

Concentration of *aniso*-(**1**+**3**-AuNS)@PSPAA used in SERS characterization:

$$C_{SERS} = 3\times2.48\times10^{-10}M = 7.44\times10^{-10}M$$

Enhancement Factors (Abased on the data in Figure 4 in the main text):

$$EF = \frac{I_{SERS}}{I_{Bulk}}\times\frac{N_{Bulk}}{N_{SERS}} = \frac{I_{SERS}}{I_{Bulk}}\times\frac{C_{Bulk}V_{Bulk}N_A}{C_{SERS}V_{SERS}N_A} = \frac{I_{SERS}}{I_{Bulk}}\times\frac{C_{Bulk}}{C_{SERS}}$$

$$EF_{avg} = \frac{155}{48}\times\frac{0.01}{7.44\times10^{-10}\times\frac{4070}{0.2}} = 2.13\times10^{3}$$

$$EF_{(47\%)} = \frac{68}{48}\times\frac{0.01}{7.44\times10^{-10}\times\frac{4070\times0.47}{0.2}} = 1.99\times10^{3}$$

$$EF_{(16\%)} = \frac{15}{48}\times\frac{0.01}{7.44\times10^{-10}\times\frac{4070\times0.16}{0.2}} = 1.30\times10^{3}$$

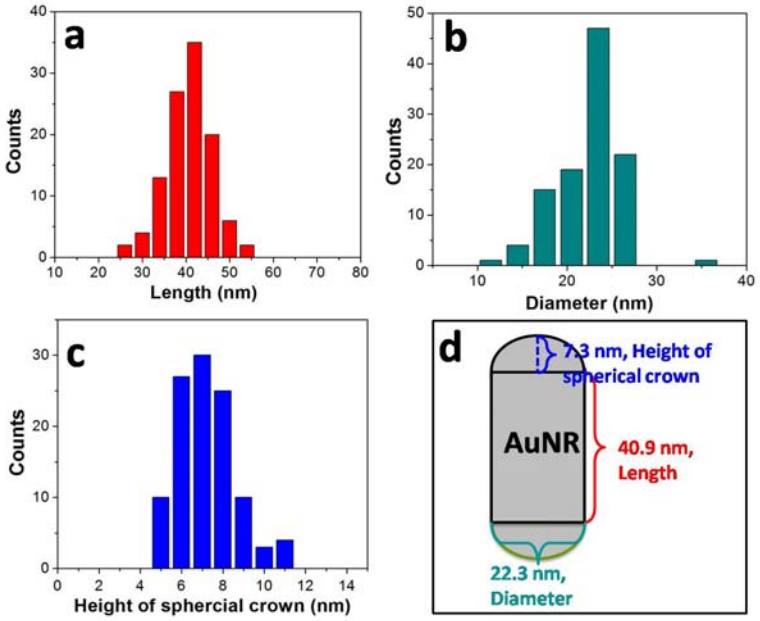


Figure S1. Statistical results of geometric parameters of the *aniso*-(**1**+**3**-AuNR)@PSPAA: a. length of the cylinder; b. diameter of the AuNRs; c. height of the spherical crows and d showing the scheme of AuNR.

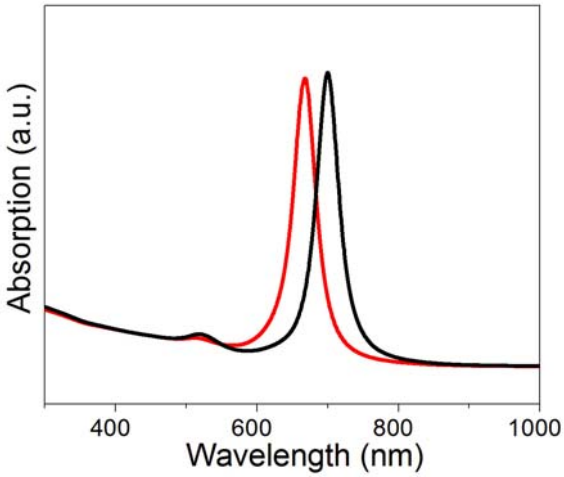


Figure S2. The FEM calculated absorption spectra of the gold nanorod without (red line) and with polymer encapsulation on the sides (black line).

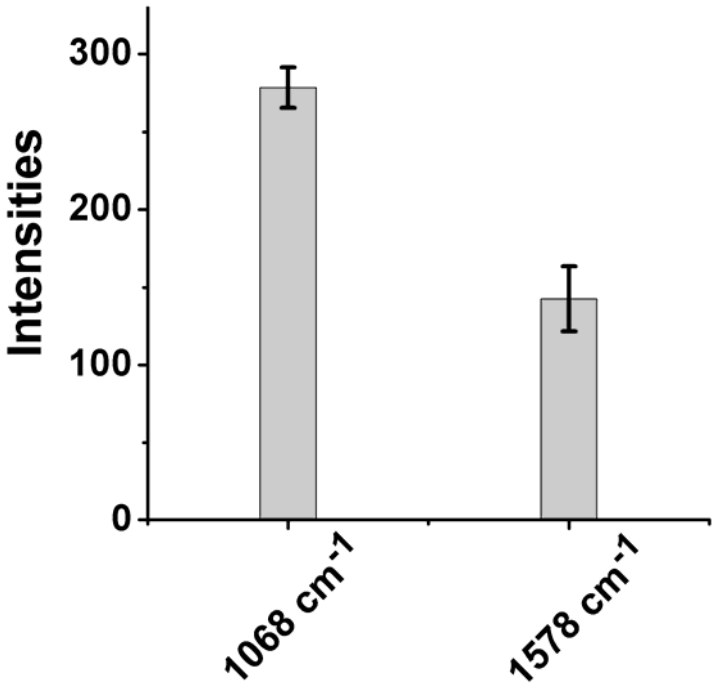


Figure S3. The standard deviation of the peak intensities of Figure 1d in main text.

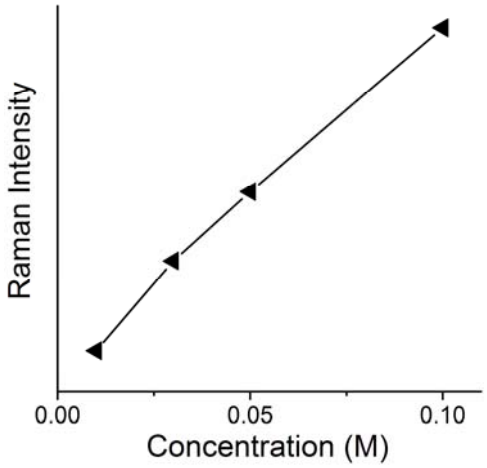


Figure S4. The dependence of Raman intensities on the concentrations of 4-MBA in 10 M NaOH solution, abased on the Raman peak at 1078 cm^{-1}.

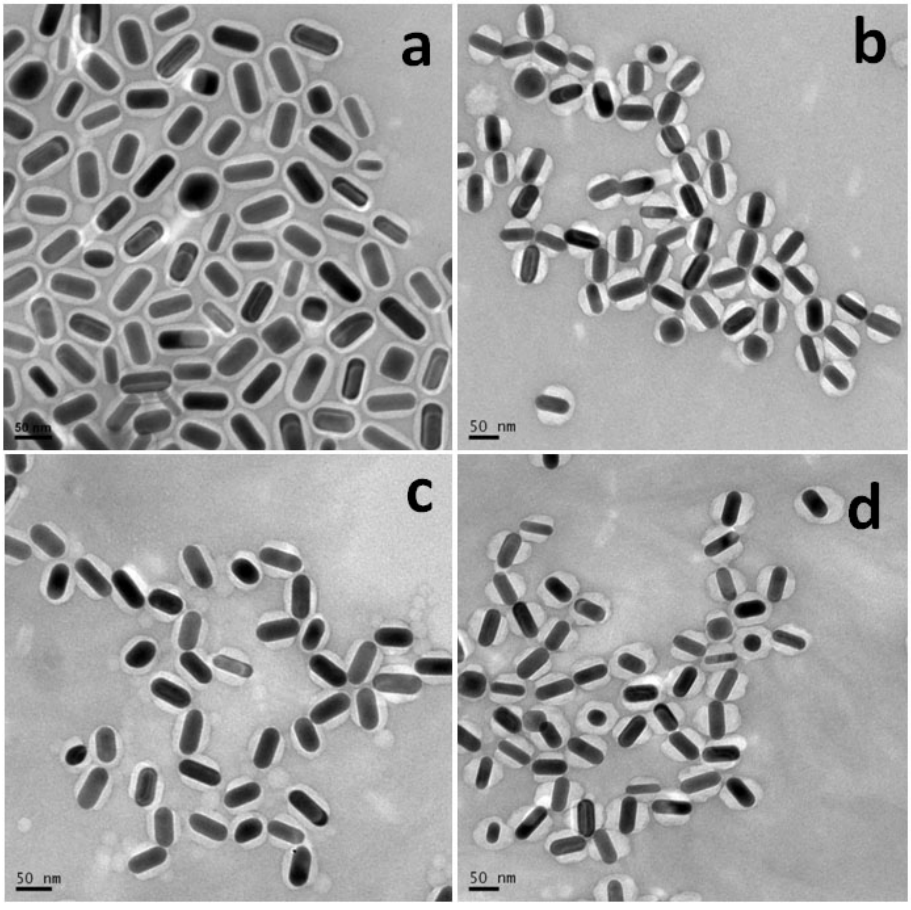


Figure S5. Typical TEM images of *iso*-(**1**-AuNR)@PSPAA (a), *aniso*-(**1**+**3**-AuNR)@PSPAA (b), *aniso*-(**1**+**4**-AuNR)@PSPAA (c), *aniso*-(**1**+**5**-AuNR)@PSPAA (d).

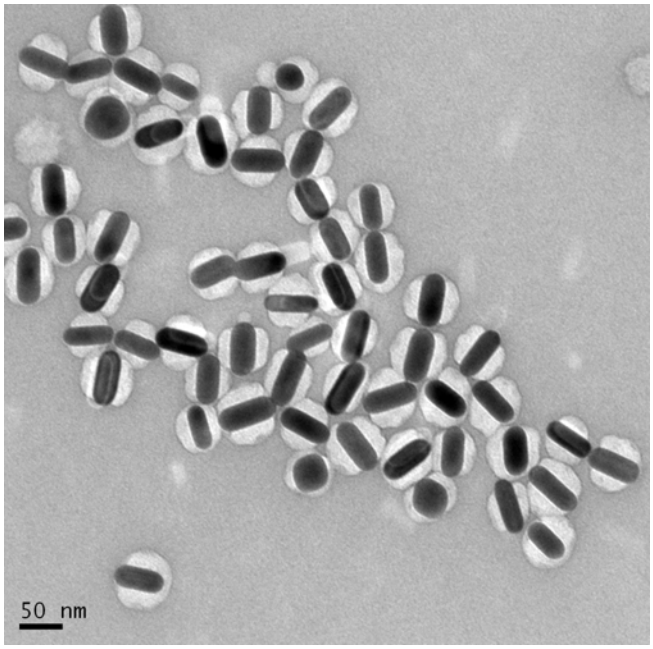


Figure S6. A typical TEM image of *aniso*-(**1**+**3**-AuNR)@PSPAA after incubation in **6** (0.01 M aqueous solution).

[1] A. Gole, C. J. Murphy, *Langmuir* **2008**, *24*, 266.
[2] G. Frens, *Nat. Phys. Sci.* **1973**, *241*, 20.